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RADIOACTIVE DISINTEGRATION APPLIED TO THE MEASUREMENT OF GEOLOGIC TIME ILLUSTRATED BY APPLICATION TO THE WILBERFORCE URANINITE.

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This paper has three parts. The first general part is by Kirsch, revised with his permission by Lane. In particular the formulae are somewhat altered in expression both to make it easier for the printer and also to put them into more familiar form for computation. There has been also some revision with reference to recent papers by A. F. Kovarik[1] of Yale University, which had not reached Kirsch at the time.

In the second part Lane calculates the age of the Wilberforce uraninite not only to show that the uncertainties as to age are not so great after all (See Fig. 1), but also to show what data are needed to reduce these uncertainties. Even now important geological results may be obtained. The third part is by Kirsch with slight modifications by Lane, and includes certain general cautions as to age calculations.

I. General Calculation of Age.

Historical treatments of the subject of this paper have already been given by Holmes and Lawson[2] and quite recently by Kovarik.[3] Holmes and Lawson based their discussion on the usual approximate formula, introducing, whenever required, one or the other of certain correction factors, which they discussed. This formula is

$$A = Pb \cdot C/(U + k\ Th) \tag{1}$$

where A is the age, C a constant, Pb, U and Th the percentage of lead respectively uranium and thorium in a mineral and k denotes the ratio between the rates of lead production from thorium and from uranium. The value and constancy of the fraction k is one of the things to be discussed. The ratio of the number of atoms disintegrating to the total number present, often expressed in terms of λ, which

[1] Science (Aug. 1, 1930) 72: 122–5; Am. Jour. Science (Aug. 1930) 20: 81–100.
[2] Am. Jour. Sci. (1) 3 (1927) p. 327.
[3] Am. Jour. Sci. 20 (1930) pp. 81–100, and Science 72 (1930) pp. 123–125.

is n/N of Kovarik's nomenclature, we will here express in terms of T which is the time required that an element shall be half gone (T_u for uranium, T_{th} for thorium, etc.) and is naturally inversely proportional to the rapidity of disintegration λ. It is $0.693/\lambda$. In terms of it

$$k = \frac{\lambda_{Th}\frac{208}{232}}{\lambda_U\frac{206}{238}} = \frac{Tu \cdot 1.156}{T_{th} \cdot 1.115} = 1.038 \cdot T_u/T_{th} \tag{2}$$

and

$$C = 1.156\,T_u/0.693 = 1.668\,T_u$$

C obviously represents the inverse value of the rate of lead production from uranium. Formula (1) is symmetrical in relation to U and Th:

$$A = \frac{Pb}{U + k \cdot Th}(1.668 \cdot T_u) = \frac{Pb}{1/k\ U + Th} \cdot \frac{1.668\,Tu}{k}$$

$$= \frac{Pb}{1/k\ U + Th} \cdot 1.607\,T_{th} \tag{1a}$$

and is thus applicable to minerals containing thorium or uranium or both elements together. When we consider, however, that the proportion of lead producing elements[1] has not remained constant through the whole period since a mineral was formed, we should bear in mind that the correction factors to this approximate formula are not identical for thorium and for uranium minerals. In fact they respectively differ very much as the difference between the age of a thorium mineral with definite "Pb ratio" ($Pb/k \cdot Th$!) and that of a uranium mineral with the same Pb ratio is larger than the difference between the true age of the former as computed from the exact formula:

$$A = \frac{T_{th}}{0.693} \cdot (2.3026 \log (1 + 1.115\,Pb/Th)$$

$$= 3.323\,T_{th} \cdot \log (1 + 1.115 Pb/Th)$$

and that calculated from formula (1).

[1] And that includes the proportion of isotopes of uranium, so that the atomic weight of uranium in Eq. 2 is not constant nor the value of k absolutely.

We should therefore like to suggest the following as one practical method of calculation for minerals in which neither of the two elements may be neglected: One calculates the terms:

$$3.323 T_u \log (1 + 1.156\, Pb/(U + kTh))$$

and

$$3.323 T_{th} \log (1 + 1.115 Pb/(U/k + Th))$$

and finds a very nearly correct value by linear interpolation in the ratio $U : k \cdot Th$ between them, *in case there is no way* of telling how much lead should be assigned to the different isotopes of *Pb*. Moreover, owing to the different values of the time average corrections, one has to fall back on interpolation formulas in dealing with any mineral rich in thorium.

Although the disintegration constants of uranium and thorium are not known with the same degree of accuracy, this is of minor importance when comparing the relative ages either of different uranium minerals or of different thorium minerals. On the other hand, the exact value of the $T_u : T_{th}$ ratio is essential even for relative determinations of age as soon as a comparison of the ages of thorium and uranium minerals inter se is involved. This leads to a discussion of the so-called constants C and k, which appear in the formulas for the age and of the disintegration constants respectively of T_u and T_{th} by which they can be replaced according to the formulas above.

II. The Constants.

We fully agree with the views of Holmes and Lawson regarding the number of alpha particles emitted per second from one gram of radium, given as $3.72\ (10)^{10}$, which has lately been repeatedly confirmed but we find it necessary to subtract a correction from T_u as calculated indirectly from T_{Ra} and the $Ra : U$ ratio $(3.40\ (10)^{-7})$ in order to allow for the branching off of the actinium series. If we assume a branching ratio of three percent[1] T_u should be decreased by three percent since only 97 percent of the U contributes to the Ra and we therefore get:

$$T_U = 4.3\ (10)^9 \text{ years} = 4.3 \times \text{antilog } 9 \text{ years} \qquad (5)$$

[1] Hevesy in Science, Nov. 21, 1930, says this is fixed, and this has been the general result of experiments. But confer Kovarik (Am. J. S. LXII, p. 125) and James E. Wildish (Jour. Am. Chem. Soc., Jan. 1930, p. 175). Also Grosse and Kurbatow report the actinium radium ratio in the Wilberforce uraninite as four percent (pri. com.)

and

$$C = 7.175 \times \text{antilog } 9 \text{ years} \qquad (6)$$

It should be remembered, however, that in this case we are including all U, both Urradium (U 238+) and Uractinium (U 239) and that T_u thus obtained is an average figure. It will be very desirable to get the disintegration ratio of the uranium of the kolm which gives such pure radium lead (At. wt. = 206.01)[1] although it seems not probable that it will give a materially different value of T_u.

Again, as regards the disintegration ratio of thorium and its half life T_{th}, we are not yet prepared to accept the value based on the scintillation counts by Rutherford and Geiger, which is extensively used, since it is at hopeless variance with certain results from mineral analyses. One can (as one of us has already explained elsewhere)[2] derive a value for the ratio of the disintegration constants of uranium and thorium from the composition of such radioactive minerals as contain both elements in comparable quantities (table I) or rather in quantities corresponding to comparable rates of lead production, provided that the amounts of both kinds of lead RaG + and ThD actually present in the minerals have been found by atomic weight

TABLE I.—Analyses of Thorium Uranium Minerals.

	Thorianite			Thorite	
	I	II	III	Ceylon	Brevik
Kovarik's No. A. J. S., 1930, p. 90	9	10	11		2
Uranium %	11.8	20.2	26.8	1.62	0.45
Thorium %	68.9	62.1	57.0	54.4	30.10
Lead %	2.34	3.11	3.5	0.36	0.35
At. Weight of lead	207.27	206.91	206.84	207.77	207.90
† $RaG^* : U$	0.0815	0.0861	0.0780	0.0282	0.0474
$ThD : Th$	0.0200	0.0218	0.0246	0.0058	0.0109
$\frac{\dagger RaG^* : U}{ThD : Th}$	4.07	3.95	3.17	4.86	4.35
k	0.246	0.253	0.315	0.206	0.230
$\lambda u/\lambda th$ after Kovarik:	3.78	3.68	2.91		3.50

† RaG^* means here all lead derived from Uranium.

[1] Baxter and Bliss, Jour. Am. Chem. Soc. 52 (1930) 4848.

[2] Wien. Berichte, Vol. 131, p. 551 of 1922; Mitt. Inst. f. Radium Forschung, No. 150.

determination, and provided there has not been selective removal or addition of these elements.

The values of k are not exactly the reciprocals of those given by Kovarik in his table II, partly because there has not been used[1] the even atomic weights, e. g., 206, but the most accurately known (at present) which allow for a packing factor, e. g., 206.05 and 208.02.

The average value of k, however, that we get (0.25) differs very widely from that used by Kovarik based on scintillation counts (0.38) by an amount largely in excess of the margin of error in the analytical results.

A conclusive proof of the correctness of the value $k = 0.25$ seemed[2] to be offered by the first analysis of thorianite made by Hönigschmid. For here, assuming the atomic weights of uranium lead and of *ThD* to be known, we know the exact value of the ratio between the two sorts of lead present in the analyzed specimen, since by lucky chance the ratio to be inferred from the proportions of *U* and *Th* present, happens to agree with that corresponding to the atomic weight of common lead. Therefore the content of the latter is not significant in the calculation of the ratio of uranium lead to *ThD*.

As Holmes has suggested, we find that an attempt to maintain the old value of k (0.38) leads into a serious conflict with ascertained analytical results.

There still exists, however, a possibility of doubting the disintegration constant of thorium as derived from this analysis of thorianite by assuming that the mineral might have contained originally about 6% more of uranium which has *quite recently* been lost without losing *lead* or *helium!*

However, since the arguments are not absolutely convincing a new direct determination of this important constant (k) would be most welcome. Accurate measurements of the number of alpha particles emitted per second by uranium and thorium are in progress in the Radium Institute in Vienna but will still take some time to complete, but a preliminary experiment has been made which, although attaining an accuracy of only a few percent, owing to the small number of particles counted, shows clearly that the value of the constant k lies in the vicinity of 0.25 and certainly not near 0.38[3].

We used two preparations, one containing 1.392 mg. radio-active

[1] Kirsch, Geologie und Radioktivität, pp. 150–154.

[2] Geologie und Radioktivität, p. 150.

[3] Physikalische Zeitschrift 31 (1930, Nov. 15) p. 1718.

pure U_3O_8 spread out as uniformly as possible over a disc 2 cm. in diameter, while the second preparation consisted of 2.086 mg. ThO_2 distributed over the same surface. The quantities of radioactive substances used were determined on a microbalance sensitive to 10^{-6} gm. The thorium preparation was purified from mesothorium in 1914 and should therefore lack some 18–20 percent of the equilibrium amounts of the disintegration products. This again was checked by comparison measurement of this same sample of thorium with an analyzed thorite and pitchblende of known composition.

Directly before each preparation was put a system of apertures consisting of a metal disc 4 mm. thick, which contained 12 holes of diameter 4 mm. Only a fraction of 2.25 percent of the total radiation emitted by the preparations passed through the apertures. This system was closed by a very thin foil of gold and formed one of the electrodes of an ionization chamber, while the second electrode, connected with the grid of the entrance valve of the valve electrometer, was placed at a distance 4 mm. from the first.

In 307 sec. were counted 225 α particles emitted by the uranium preparation, while the number counted without the preparation (the zero effect due to traces of contamination) was six in 117 sec. With the thorium preparation the count gave 188 particles in 276 sec., the zero effect being 19 particles in 235 sec. The net effect following from these counts was for uranium 41 particles per min., for the thorium preparation 36. Knowing that uranium emits about 2.6 $(10)^4$ particles per gram and sec. we should have expected an effect of about 40 per min. with the experimental arrangement used. This surprisingly good agreement at any rate proves that the substance was in fact spread out in a uniform manner, so that no particles were lost by absorption in the substance.

In case thorium alone without its disintegration products emits the same number of particles per gram and sec. as *UI*, we should expect from our thorium preparation 3/2 of the number from the uranium preparation per element of each series because of the greater quantity of the substance used. Further, owing to the presence of 80% of the disintegration products in equilibrium with thorium themselves giving off particles we should expect 5/2 times the number of particles from uranium preparation (*UI UII*), finally we must add 3.5 percent because of the smaller content of oxygen in the ThO_2 compared to U_3O_8. We should therefore get

$$41 \times 3/2 \times 5/2 \times 1.035 = 159 \text{ particles per min.} \qquad (5)$$

Now our thorium preparation yields only 36 particles per min., that is 4.4 times less than the value 159. From this it follows that the disintegration constant of thorium is about $4.4 \cdot 232/238$, i. e., 4.3 times smaller than that of uranium and furthermore that k, the ratio of the rates of lead production of both the elements must be roughly 0.24. Again if the thorium should happen to contain traces of ionium or on the other hand hold more than 80% of its equilibrium quantity of disintegration products—for it cannot contain less—this would lead to a still smaller value of k!

On the whole, we can say that a reasonable agreement exists between these direct measurements and the calculations from the mineral analyses above. Rutherford and Geiger in their classical pioneer work on this subject do not claim a high degree of accuracy; their paper contains no description of the way in which the thorium was prepared, nor are the results of measurements on thorite films mentioned or discussed.

Pending more accurate measurements, we are thus entitled to assume as the values most suitable for calculating the ages of minerals:

$$C = 7100 \quad \text{and} \quad k = 0.25$$

and accordingly, for the interpolation method before mentioned, the half lives:

$$T_u = (.693/1.62 = .428)10^{+10} = 4.28 \times \text{antilog } 9 \text{ years} \qquad (7)$$

and

$$T_{th} = (.693/3.9 = .18)10^{+11} = 1.8 \times \text{antilog } 10 \text{ years} = 18 \times \text{antilog } 9 \text{ years} \qquad (8)$$

in remarkable agreement with the measurements of H. N. MacCoy who found $T_{th} = 1.78 \times$ antilog 10 years (Phys. Rev. (2) 1 (1913) p. 403); cf. also B. Heimann Wien. Berichte *123* (1914) p. 1369, and L. Meitner Phys. Zs. 19 (1918) p. 257. The U in eq. 7 includes all the U isotopes.

PART II.

Application to Wilberforce Uraninite.

Canada has for years been famous for its pegmatites and pegmatite minerals on which H. V. Ellsworth has done such fine work[1] and more recently H. S. Spence.[2]

[1] Canada Department of Mines, Summary Report 1921, Part D, and the American Mineralogist, a number of papers.

[2] American Mineralogist, Sept. Oct. 1930,—Also Dec.

Special attention has been given by Ellsworth to those minerals to which one might look for sources of radium, and recently deposits approaching the commercial have been found.

Years ago, Lane presented a discussion of the possible solution of Laurentian (pre-Cambrian) problems by means of the relative age of minerals, estimated by the extent to which the disintegration of uranium, thorium, actinium and radium to lead had gone on. Some recent newspaper notices[1] have rather overestimated the exactitude with which such estimates may be made (1852 million years), and Hevesy's recent lecture,[2] being to a general audience, is a bit too positive.

It is the object of this section to show by application to the Wilberforce uraninite that though there are uncertainties and greater exactitude is much to be wished for and is indeed in sight, one can obtain results already which are of geologic value, and the facts and research needed for closer estimates will be pointed out.

Thanks to H. V. Ellsworth and the officers of the Ontario Radium Corporation the committee on the Estimation of Geologic Age by Atomic Disintegration were enabled to purchase some twenty pounds of excellent material for research. This had already been analyzed three times so that it has as yet been deemed needful to analyze the material used for atomic weight determination only for *U*, *Th*, and *Pb*. H. S. Spence and R. K. Carnochan have described the occurrence fully and given two of the analyses early in 1930.[3] So we need give only a third analysis made more recently by H. V. Ellsworth and the figures for *U*, *Th* and *Pb* obtained by Wells on the very same material as that from which the atomic weight of the lead was determined, as follows:

Sp. G. = 9.062 at 20°.57

UO_2	39.10
UO_3	32.40
ThO_2	10.60
PbO	10.95
CeO_3	1.88
Y_2O_3	2.14
Fe_2O_3	0.43
Al_2O_3	0.09

[1] Boston Post, Nov. 23, 1930, p. 11 of color-feature section.
[2] Science Nov. 21, 1930, p. 509.
[3] Transaction Can. Inst. Mining and Metallurgy for 1930.

SiO_2	0.19
CaO	1.01
MgO	0.08
MnO	0.03
H_2O	0.05
H_2O at 100°	0.65
	0.31
	100.06

The *U. Th. Pb* were:

	I E. W. Todd	II H. V. Ellsworth altered	III H. V. E.	IV R. C. Wells
U.....	60.56	55.26	61.44	53.52
Th.....	10.02	11.92	9.32	10.37
Pb.....	9.65	10.25	10.19	9.26
$Pb/U + 0.25Th$..	.153	.176	.16	.165
Age in millions of years.....	1092	1258	1142	1178

Using the formula and the constants above given equation 1 becomes

$$\text{Age} = 7.14 \times \text{antilog } 9 \text{ years} \cdot \frac{Pb}{U + 0.25\,Th} \qquad (7)$$

and the various analyses give the figures for the age of the last row. Following the suggestion given above (p. 359), analysis IV gives an age to be interpolated between 1090 and 1160 years.

We see that the approximate formula gives us ages between 1100 and 1300 million years. But we can make a closer estimate than this, since Baxter and Bliss have determined the atomic weight of the lead of Analysis 4[1] as 206.19(4). We can tell about how much of the lead is derived from Radium, how much from thorium, etc. Kovarik assumes four kinds of lead

Pb(206) *RaG* from Radium
Pb(207) *AcD* from Actinium
Pb(208) *ThD* from Thorium
Pb(207.2) ordinary lead. E. g. (*Pb* 209).

But there are also possibilities of other leads, and ordinary lead has been shown by Aston to consist of all three leads *Pb*(206) (207) and

[1] Journal Am. Chemical Society (Dec. 1930) 52: 4852.

(208), part of which may be thought to have formed from *U* and *Th* before the uraninite was crystallized. It can be shown that there is but little of this ordinary lead in the Wilberforce Uraninite anyway, however:

(1) In the first place, by the atomic weight of the lead which is so largely *RaG*, corresponding to the large amount of *U* in the mineral.

(2) In the second place, an x-ray examination by John T. Norton shows only the lattice of UO_2, 5.45 Ångstrom units, which would not be likely if there were much original lead.

(3) In the third place, the amount of extra oxygen as shown in Ellsworth's analysis by the UO_3 is ample to consider the *Pb* as having been derived from UO_2 with *O* set free in accordance with Ellsworth's autoxidation theory. No original lead is needed.

(4) In the fourth place, the amount of *He* is the highest Bennett and Moore have found (10.39 cc per gram, p. 372, below), and this again points to a large amount of radioactive lead.

(5) As will be seen, whatever values we take for *k* or for the amount of actinium lead, there must be some actinium and thorium lead and to that extent the possibilities of ordinary lead are diminished.

(6) There is a sixth check theoretically possible which has not yet been made.

Whenever lead is separated from a mineral like uraninite there are isotopes of lead which are radioactive separated with it.

RaB, half gone in 26.8 minutes; the quantity in equilibrium with 1 gram *U*. 1.02 antilog—14 grams.

RaD, half gone in 22 years; the quantity in equilibrium with 1 gram *U*. 3.1 antilog—9 grams.

AcB, half gone in 36 minutes; the quantity in equilibrium with 1 gram *U*. 2.5 antilog—17 grams.

ThB, half gone in 10.6 hours; the quantity in equilibrium with 1 gram *Th*. 6.41 antilog—14 grams.

These are in too small quantities to be recognized by ordinary chemical methods, but they could be recognized by the electroscope and by very prompt repeated examination of the decay curve an idea as to whether the actinium series was at present contributing a substantial amount as a check on direct actinium determinations.

The proportion of protactinium to radium[1] is not yet determined. On that James E. Wildish and A. V. Grosse are at work. Grosse and Kurbatow report actinium to radium as four percent.

[1] Cf. Jour. Am. Chemical Soc., Jan. 1930, p. 175.

(7) Finally there is the consistency of the age results obtained with the geological conditions and the age of other minerals. But of course in applying this test there is great danger of reasoning in a circle.

These minor methods should and will be left to the last.

Grouping all the lead that is not *RaG* and *ThD* formed since the mineral crystallized, together as y we have

$$RaG + y + ThD = 9.26 \tag{8}$$

We include in y: (1) Any actinium lead; (2) Any *RaG* and *ThD* formed before the mineral crystallized and present in solid solution, not a result of the decomposition of the uranium and thorium segregates in the crystallization of the mineral; (3) Any ordinary lead or *Pb*(209) that may be present; and (4) The insignificant amount of *RaB*(214) *AcB*(213?) *ThB*(212) and *RaD*(210).

From the atomic weight of the lead we shall have:

$$\frac{RaG}{206} + \frac{y}{207} + \frac{ThD}{208} = \frac{9.26}{206.195} \tag{9}$$

There is a question here whether we should take an even 206 or allow for a packing effect. Hönigschmid hardly thinks that the determination of the atomic weight of *Ra* should put it down to 205.95, and the atomic weight of the kolm lead 206.01 may be expected to have something subtracted for actinium lead. There is an uncertainty of about .01 which becomes of considerable importance if we eliminate *RaG* and determine *ThD*. Eliminating *ThD* from these two equations, we can get

$$RaG = \frac{206}{2}\left(9.26 \cdot \frac{1.805}{206.195} - \frac{y}{207}\right) = 8.3493 - y(.4976) \tag{10}$$

$$ThD = 0.910 - (.5024)\, y \tag{11}$$

Whence *ThD* cannot be greater than 0.91, since y is not less than 0, and y cannot be greater than 1.82 — and this y must include both *Act.D* and any ordinary lead. Thus *RaG* must be between 8.3473 and 7.44. (Fig. 1.)

These equations are nearly like those used by A. Holmes in Nature, Sept. 6, 1930. If we can add one more equation, the equations can be solved definitely and then by equations given below we could get the age in three ways. If we can assume either that y is all *Act D* and

for instance three percent of *RaG* or that as Holmes assumes *ThD* is 0.38 or .25 of *RaG* + *y* or of *RaG*. But none of the uncertainties as to how much of *y* there is or what its atomic weight may be can effect the maximum value for *x*. It cannot be more than 8.3492. The

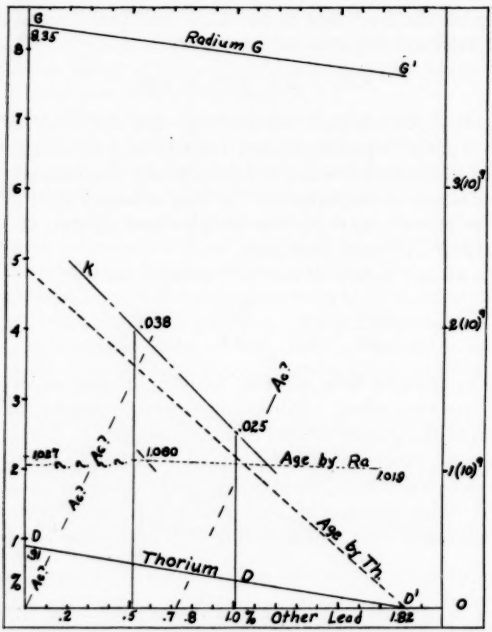

FIGURE 1. Illustrates the computation of all possible ages of the Wilberforce uraninite consistent with the amounts of uranium, thorium and lead and the atomic weight of the latter. Possible amounts of lead not derived from radium are laid off as abscissas. Full lines join the tops of the ordinates which show the Radium G and Thorium G that correspond and the scale is on the left. Lines with dashes show the ages corresponding. Their scale is on the right. The relative lead producing capacity of thorium to uranium is shown by the line marked *k*.

minute we assume, however, a rate of production of thorium or actinium, its value becomes definite. But instead of beginning with any such assumption, we plot the values of *RaG* as ordinates with the various possible values of *y* as abscissas (Fig. 1). The exact atomic

weight of y to be taken whether 207 or 207.2 will make but a very slight difference in the slope of this line. In view of the age which we shall find must come to the mineral under any supposition, and the fact that there is certainly some thorium lead and actinium lead and plenty of oxygen for autoxidation as Norton has shown and the original UO_2 lattice is unaltered, we believe we have been safe in agreeing with Kovarik[1] for similar minerals, that the lead is practically $Pb206$ or $Pb207$ or $Pb208$ and in using 207 for the denominator of y. It must be remembered, however that in estimating the age if we assume y to be all actinium lead we may make a more substantial error and gét the age too high or conversely.

In Fig. 1 with $Pb207$ as abscissas, the lines representing the corresponding properties of RaG and ThD are straight.

If we assume that there is a factor k as used in equation (1) of part (1) such that the age so obtained will be the same as that obtained from the quotient of RaG/UI, then if UI is urradium the parent of radium and AcU the parent of Actinium $U = UI + AcU$

$$\frac{RaG}{UI} = \frac{Pb}{UI + AcU + kTh} = \frac{RaG + y + ThD}{UI + AcU + kTh} \tag{12}$$

In equation (12) it is assumed, as in equation (1), that AcU is so small that a factor, call it j, dependent on the relative rate of disintegration of UI and AcU need not be introduced. If it is, then in equation (14) we must write $jAcU$.

$$\frac{AcU + UI + kTh}{UI} = \frac{RaG + y + ThD}{RaG} \tag{13}$$

$$\frac{AcU + kTh}{UI} = \frac{y + ThD}{RaG} = \frac{Pb - RaG}{RaG}$$

$$\therefore k = \frac{UI \cdot (Pb - RaG)}{Th \cdot RaG} - \frac{AcU}{Th} \tag{14}$$

The last term will often be small. If we neglect it and if we take k as having a value 0.25 or 0.38, we will find certain values of ThD and RaG are implied. So then we have another curve Fig. 1 for values of k, and we may pretty surely assume that k lies between 0.38 and 0.25. Piggott has pointed out that according to this test, Aston's estimates

[1] Science, Aug. 1, 1930, p. 122–125.

of the isotopes in Bröggerite lead are substantially out. Aston did not claim high accuracy.

Now as to age we may rewrite Kovarik's equations[1] which are essentially the usual ones,[2] using decimal logarithms instead of exponentials and the weights actually found in analysis rather than numbers of atoms, and the half lives instead of the disintegration constants, as follows:

Age by uranium in millions of years

$$= 14{,}290 \log \left(1 + 1.156 \frac{RaG +}{U - AcU} \right) \quad (15)$$

This is if we use for the half life of uranium a value (4300 million years) which allows for the amount of actinium supposed to be in uranium, and the proportion of disintegration in a given time that is supposed to belong to it. In the ordinary chemical analysis it is not possible to separate the U which changes to radium from that which changes to actinium. If we assume that the Ur-radium parent of radium has an atomic weight of 238.07 and the Ur-actinium is U_{239} and that ordinary uranium has an atomic weight of 238.14, then[3] about six percent of the U is U_{239} and we should have

$$U\ 238.08 - AcU = .94 \cdot (53.52) = 50.3 \quad (16)$$

$$\text{Whence Age} = 14{,}290 \log. \left(1 + 1.156 \frac{RaG}{50.3 + \text{some part of } 3.2} \right) \quad (17)$$

When we make RaG as great as possible in the equations above, there would be no AcD, hence no Ur-actinium, and we should have

$$\text{Age} = 14{,}290 \log. (1 + 1.156 (8.349/53.52)) \quad (18)$$

(in millions of years) = 14,290 log. (1.180) = 1027 million years if $y = 0$. Or assuming T_u is not reduced for the proportion of actinium it would be 45/43 greater, i. e. 1075 million years. On the other hand,

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[1] Am. J. Sci., 1930, p. 98.

[2] Geologie und Radioktivität (p. 129)

[3] Geologie und Radioktivität (p. 138). The usual atomic weight of U is given as 238.17, but 238.14 is the latest by Hönigschmid, used in his new edition of Landolt–Börnstein's tables. It will be interesting to know the exact age and source of the different uraniums, as the proportions of Uractinium may differ.

when we assume that all the y lead is Ac-lead, an obviously impossible value since thorium is present, we may then have, as a maximum

$$\begin{aligned} \text{Age} &= 14{,}290 \log. (1 + 1.156\ (7.59/50.3)\ ) \\ &= 14{,}800 \log. (1.175 = 1050 \text{ million years} \end{aligned} \tag{19}$$

For intermediate values we may assume $U(238)$ to be 50.3 as soon as we have $y = .322$ and we have, assuming $U(238) = 50.3$ (by slide rule)

and $y = 5$ and 1.0, the ages (20)

1061 and 1031 million years respectively.

Now as tó the age by the thorium ratio, if we have

$$\text{Age} = 3.323\ T_{th} \log. (1 + 1.115\ (ThD/10.37)\ ) \tag{21}$$

(In millions of years) = 59,800 log. (1 + 1.115 (0 to .91) (10.37)).

Then the range must be from 2400 million years (if $ThD = .91$ as shown in the figure 1) down, and if we assume $y = 1$ $ThD = .408$; $RaG = 7.85$; $Th = 10.37$ and U is 53.52 to 50.3 and $k = ThD.U/Th.$ $RaG = 24.8$ to 26.8—consistent with what was found in Part I.

As to Actinium, Kovarik, following Aston, makes its rate of decay such that $Tacu = 2.7 \times$ antilog 8 years.

But if about four percent of the atoms disintegrating are actinium while six percent of the uranium is the percent of uractinium, the rate of disintegration must be less rather than more, and A. Holmes came to the same conclusion (Nature, Sept. 6, 1930).

We can give more definite figures when Baxter has determined the atomic weight of the very same uranium. But to show how the calculation would be:—

If the actinium lead is three to four per cent of the radium lead, i. e., 0.27 (about a third of y) and *if* the rate of decay of the Ur-actinium (239) is two thirds that of the uranium and *if* the percent of Ur-actinium is about six percent of the U since the half life of Ur-actinium would be three halves that of $U(238)$, then

$$\begin{aligned} \text{Age} &= \text{about } 22{,}000 \log. (1 + 1.153 \times .27/3.22) = 22000 \times .04 \text{ to } .06 \\ &= 880 \text{ to } 1320 \text{ million years} \end{aligned}$$

Very possibly the checking of the age may be the most accurate control of the rate of decay of the $U239$. If all the y is actinium lead, we should have to reduce the half life more to get accordant ages, but the half life assumed by Kovarik would not agree at all with any reasonable suppositions. If we assume that all the y is Pb and that

one-sixth of the U is $U(239)$ and there cannot be much more, then with the half life assumed, we should get 1420 million years.

It is not worthwhile to go into further detailed calculations. But we can see how unlikely it is that the decay of the original ur-actinium should be as rapid as Rutherford and Kovarik assume, and we see the import of the work upon which A. v. Grosse, Wildish and Baxter are engaged for the Committee, while we can see also that it is unlikely that the Wilberforce uraninite is 10% away from 1030 million years old. In the calculations a slide rule has been used.

We can clearly see from Fig. 1 that unless there is some great error in the data given us by the physicists, this age of 1030 million years is not far from the truth, and that when the physical data are well enough known, we shall have a triple check!

W. R. Bennett reports May 7, 1931, the following results on three 1.5 gram portions of the same sample of Wilberforce Uraninite on which the atomic weight determinations were made:

15.605, 15.543, and 15.620 cc of helium

This gives an average amount of 10.39 cc He per gram of ore. Whence (I. C. T. Vol. 1, p. 381) the ratio and age is

$$(10.39/(53.52 + 2.9) = .185) \times 910 = 168 \text{ million years,}$$

$$\text{or, (using Kirsch's } k) \; 10.37 \times .19 = 1.97) = .187$$

The age is much less than the age by the lead ratios, even when multiplying by 3 to allow for diffusion.[1] But since there is a larger amount of helium per gram than in any mineral cited in the International Critical Tables, one would naturally expect a greater amount of diffusion.

If we compare with a similar and similarly rich mineral,—the bröeggerite of Ånneröd, we find that the relations of the lead ratios, —for Wilberforce (.165), for Ånneröd (.139); and the helium ratios—for Wilberforce (.187), for Ånneröd (.14) are similar. Both indicate that the Wilberforce material is older.

III. Interpretation of the *Pb* Ratio.

By G. Kirsch.

We shall now proceed to a discussion of the important question of how the results from age determinations based on the *Pb* ratio are to

[1] Kirsch, Geologie und Radioaktivität, p. 191.

be interpreted. The radio-active minerals belonging to the pegmatite dikes from a certain region and generated during a given period of intrusion (leaving aside the question whether the intrusion period was really single or subdivided into a sequence of repeated intrusions) give as a rule the following picture:

First such minerals as have been found by X-ray analysis to possess crystal structure without having had their temperature raised to incandescence, or the Wilberforce Uraninite even give a Laue diagram, i. e., possess a crystal structure of unchanged orientation. Such minerals are found to have their ages comprised within a time-interval of about 200 millions of years. Taking a few examples, we have the Canadian pitchblendes ($Pb : U$ 0.146 to 0.179), the Ceylon thorianites (0.056 to 0.088 leaving aside some very few specimens of still greater age) or the bröggerites from Raade and Moss in Norway (0.112 to 0.148, Morogoro 0.091) Wilberforce and allied occurrences (0.15 to 0.176.) This limitation to a certain time interval we may take as established, for the very few exceptions do not necessarily belong to the main intrusion period.

One alternative view, viz. that the bröggerites are all of the same age and their different *Pb* ratios are to be explained by accidental additions of ordinary lead or chemical errors, is made less likely by atomic weight determinations with chemical analysis, notably these made by Honigschmid (206, 06). For with the same material that Honigschmid used, a considerable number of single crystals have been submitted to measurements of the *Pb* ratio with results spread over the range before-mentioned. Another alternative explanation is that the lead has been extracted from these minerals to a variable extent. But these are analogous variations shown by thorianites from Ceylon. The large amount of helium contained in these latter minerals makes it most improbable that they should have been altered to the requisite extent. Another argument against this second explanation is the subdivision of the bröggerites according to their *Pb* ratios into well-defined groups[1] as such a distribution must necessarily have been effaced even by slight alterations.

Summing up, we may say that the minerals here considered must be assumed to have ages corresponding to the values found for their *Pb* ratios.

In any case, we must not assume that the age thus defined is identical with the age of the pegmatite dike in which the mineral was found.

[1] Forschungen und Fortschritte, 10 Nov. 1929, p. 372.

For, as has repeatedly been shown, minerals from the same locality, which may be assumed to have been found in the same dike, give age values differing considerably from each other, as is indicated in the following table.

TABLE II.—Bröggerites from Karlshus.

	Pb ratio
1. Anal. C. N. Fenner and C. S. Piggot	0.129
2. Anal. E. Gleditsch	0.137
3. Anal. E. Gleditsch	0.133
4. Anal. W. Riss	0.125
5. Anal. W. Riss	0.129
6. Anal. W. Riss	0.138

We must then either assume (that the analytical methods are accurate only to some ten per cent or) that bröggerite crystals may be generated during large intervals of time while the pegmatite dike has solidified (or that there is a zonal variation in composition and the material analyzed is not from the same zone), or we have to ascribe a greater age to the crystals than to the dike itself. They must therefore have been formed beforehand at different times and at greater depth and have been carried upwards with the molten magma when the dike was formed. The ages of the different crystals then would only signify at what times the magma was fluid and for the present nothing else.

A second group of minerals, silicates and other salts where the anion is the radical of a weak acid, which under the action of the radio-active rays are transformed into amorphous glassy substances in the so-called metamict state, give *Pb* ratios that range from the highest values found with the former group down practically to zero. Thus for example minerals of this type from Ontario in Canada have given the *Pb* ratios 0.014, 0.023, 0.024, 0.030, 0.035, 0.042, 0.046, 0.088, 0.115, 0.149, 0.158, 0.198; again there are thorites from Ceylon with the *Pb* ratio 0.024, 0.043, 0.063, 0.094.

Furthermore, the minerals of the thorite type from the Middle Devonian at Brevik, Norway, known from Holmes' and Lawson's investigations belong to this group.

We turn to the possible interpretations of the variability in the *Pb* ratio amongst the minerals of this second group. The assumption that for these thorites the age should be taken equal to that calculated from the actual value of the *Pb* ratio involves very serious difficulties

as has already been stated by Holmes. Thus one would have to postulate that the surges of hot solutions which at intervals of time may be assumed to have passed through the dikes as veins have carried a certain, not too small, amount of dissolved thorium, and, displacing other crystalline matter, have deposited large single individual crystals of thorite, etc. However, as the thorites considered are unable to regenerate their crystal lattices, once they have been destroyed by the action of the rays, one can hardly ascribe to them this faculty of displacing other crystallized substances. Considering also, that quite often crystals are found having an age equal to that of the oldest minerals in the first group and therefore of an undoubted magmatic origin, one can hardly avoid the conclusion that the minerals of the second group are practically all of them quite as old as those of the first group. Besides, if one should accept the admixture of ordinary lead in a variable amount to the crystals of the second group as an explanation for the variability of their *Pb* ratio, one would be led to the improbable conclusion that all minerals of this kind all over the earth should be considered of quite recent formation.

It must always be remembered that ordinary lead is a stranger to the pegmatitic dikes. In those cases where the atomic weight of the lead in such minerals has been determined (note the two thorites in Table I), the results are in favor of a purely radio-active origin.

We have now to discuss as a last alternative the explanation of Ellsworth that the differences in the *Pb* ratios of the metamict minerals are due to losses of uranium or lead in variable amounts. In this connection it should be noticed that, even though the interiors of many crystalline phases are not accessible to the different mineralizing agencies occurring in the dikes, this is not necessarily the case with the amorphous phases, indeed the opposite may be assumed as true. Further, it seems obvious that especially lead, which apart from helium is the only substance falling out of line with those other elements which have spontaneously crystallized together, will be extracted in the first place.

Bearing in mind that the physical conditions (temperature) which may lead to a revival of pneumatolytic or of hydrothermal activities within a dike, owing to the large dimensions of the system considered and owing also to the low thermal conductivity, must change very slowly indeed, it seems obvious that the span of time during which the crystals are liable to undergo chemical changes must be counted in

hundred thousands if not in millions of years. Now the immense length of time with which we may here count makes it very probable that the possible reactions will proceed until a certain final state of equilibrium has been attained. This view is also supported by the remarkable similarity in composition of such metamorphosed minerals derived from the most different localities. Thus an analysis of the gummite from North Carolina proves its content of silicon dioxide to be five percent, whereas the water content is 10.5%[1] and for the gummite from St. Joachimstal the same results are found. Also the gummite from Katanga has the same water content. The water content of thorites is generally between six and seven percent whether they are from Scandinavia, from Asia Minor, or from Ceylon (Doelter, Hb. d. Min.-Chem. III, p. 228, anal. 2–7) whereas the uranothorites have in general 11 to 12 percent of H_2O (l. c. anal. 9–13). It is therefore probable that under the action of chemical agencies a metamict mineral may readily move its lead. Granted this, the age found for a certain metamict mineral would simply denote the length of time elapsed since chemical agencies were last active having free access to the crystal in question.

Summing up the contents of the proceeding paragraph we may say: In the values found for the *Pb* ratio in non-metamict minerals (oxides, salts of strong acids with a crystalline structure), we have in all probability indications of magmatic activity in the depth at the corresponding times. On the other hand, the *Pb* ratio of metamict minerals (salts of weak acids) indicates the time when the last pneumatolytic or hydrothermal activity occurred.

So far we have only dealt with pegmatite minerals. Now there are also radio-active fissure minerals of pneumatolytic or hydrothermal origin, to which we may apply the conclusions drawn from the preceding reasoning. The *Pb* ratio for such minerals, whether they are pitchblendes or metamict minerals must necessarily correspond to epochs of increased activity and mineralization in the dikes. However, as an increase in the dike activity in pegmatites as well as in fissure must be taken as a sign of increased magmatic activity in greater depths, one must infer that the ages of radio-active minerals in the large majority of cases are to be considered as a sign of magmatic events occurring at the times derived from these data.

[1] See paper presented to the Mineralogical Society at the Toronto meeting, 1930, by E. P. Henderson, E. Posnjak, and C. S. Ross, Am. Mineralogist, 1931, p. 213.

Relationship Between Radio-Active Age Determinations and the Stratigraphic Time Scale.

The task of fitting in a pegmatite dike into the stratigraphic time scale does not fall on the physicist but on geologists. We shall here limit our discussion to a brief indication of how the age of pegmatite dikes can be estimated from the age of the minerals it contains.

Taking as an example the pegmatite dike at Divino de Uba in Brazil, from which the two minerals investigated by C. N. Fenner, monazite and samarskite, were derived, we may say that most probably its age is at least that of the samarskite and certainly not greater than that of the monazite. Its actual age cannot be more exactly defined than by these limits, for the monazite might possibly have been injected with the magma as a preformed crystal, whereas the samarskite, being a metamict mineral, may have been subjected to mineralizing influences during a later period, in the course of which part of its lead may have vanished. Possibly more exact estimates of the age might have been derived from a closer examination of its paragenesis, provided the sample affords any information of this kind. Thus if the monazite should prove to be intergrown with minerals undoubtedly formed during the solidification of the dike, or else to show arrest of growth due to such minerals, one would infer that the age of the dike coincided with that of the monazite.

Turning again to the pegmatite dikes of the Fredrikshald granite, the age of the dike at the Karlshus quarry cannot be taken as greater than that which corresponds to a *Pb* ratio of 0.125 : vide Table II. Bröggerites found at Annerod have given *Pb* ratios of 0.136, 0.124, 0.124, and 0.112. Provided all these crystals were obtained from the same dike, its age cannot be higher than the *Pb* ratio 0.112 indicates. Only in cases where from one and the same dike ten or more crystals from non-metamict minerals have been analysed can its age be stated with an accuracy of a few percent. Either the age is equal to that of the youngest mineral it contains or may be some few million years younger. That dikes differing in age by quite considerable amounts exist near Fredrikshald is not altogether impossible. In the majority of cases the dikes were most probably formed already at a period indicated by the *Pb* ratio 0.012, whereas a few dikes containing bröggerites may have been formed at a period later in time, possibly as late as the upper Paleozoic age, although these intrusions seem, so far, not to have been laid bare by subsequent erosion.

We cannot well take an intrusion to have remained in the fluid

state for as long a period as 200 million years (the span of differences between indicated ages of different bröggerites). The formation of these bröggerites therefore may have occurred at recurrent epochs of liquidity. In the course of such repeated fusions leading to differentiation, the conditions for the formation of bröggerites must be expected to show systematic variations. This is borne out by the analyses of the bröggerites. The oxygen content is liable to change, rising from the oldest to the youngest crystals as is seen from figure 2,

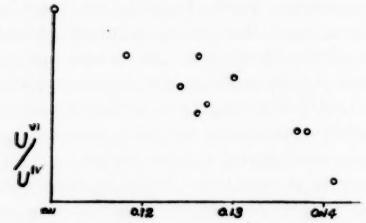

FIGURE 2. Oxygen content indicated by U^{VI} to U^{IV} and lead uranium ratio indicating age of the bröggerites.

where the ratio $U^{VI} : U^{IV}$ is plotted against the *Pb* ratio. This is the reverse of the effect of autooxidation! Here the lead is brought in as uranium corresponding to the original composition of the mineral. Also the thorium content falls from the oldest to the youngest bröggerites: Among some 60 analyses 11 have $Th : U$ 0.12 all of which have $Pb : U > 0.130$; three analyses gave $Th : U$ 0.01 with the *Pb* ratio 0.112, 0.118, 0.125. Further this decrease in the thorium content is not regular: from a maximum at $Pb : U$ 0.139 the thorium content falls steadily to a minimum at $Pb : U$ 132 rising again abruptly to a new maximum at $Pb : U$ 0.131 falling again to a second minimum at $Pb : U$ 0.125. Outside these limits the number of analyses is too restricted to allow of any definite conclusions regarding a similar periodicity, which is nevertheless intimated. Regarding the distribution of the bröggerites over different *Pb* ratios, the following remarks should be made. After a certain period of time from which only a few crystals have been analyzed the formation of bröggerites seems to make a vigorous start at the value $Pb : U$ 0.139 and goes on with at least two culminations down to the value $Pb : U$ 0.125 after which again a few crystals are spread out over a larger interval of time.

The only other region from which a large number of radio-active

crystals of the same species have been analyzed (some 20) is Ceylon, where the thorianites investigated may really be considered as pitchblendes abnormally rich in thorium. As far as can be judged from this limited material the same facts that were found with the bröggerites are again found here. Following on a few single crystals of greater age, we notice a formation of thorianites on a larger scale lasting over a span of time comparable in length to that found with the bröggerites. Within this interval a decrease in the $Th : U$ ratio is found to occur twice. Finally there are again a number of single crystals spread out over a larger span of time as with the bröggerites. Among these last named thorianites there is in analogy with the three bröggerites of abnormally low thorium content an example of thorianite of exceptionally low thorium content, i. e., a pitchblende having only 7.8 per cent *Th*. Thus these results offer a very close analogy to those obtained with the bröggerites from the Fredrikshald granites saving a general shift of the ratio $Th : U$ to higher values differing from the former in a ratio of about 10 : 1. One can hardly avoid the conclusion that this fact must be due to a low content of uranium in the magma, as has already been found by Smeeth and Watson working with rocks from Mysore.[1] This is probably characteristic also for Ceylon possibly also for Madagascar and Mozambique.

The next step to be taken will be to study on a broad basis all analogous occurrences. In this paper we hope to have shown how far distant we are still from an accurate (i. e., within the limits of several tens of million years) correlation between stratigraphic and radio-active chronology, while yet in a broad way the ratios are useful and reliable.

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[1] Phil. Mag. (6) *28*, 44, 1914; *35*, 206, 1918.